Thermodynamics of enhanced heat transfer: a model study

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Situations where a spontaneous process of energy or matter transfer is enhanced by an external device are widespread in nature (human sweating system, enzyme catalysis, facilitated diffusion across bio-membranes, industrial heat exchangers). The thermodynamics of such processes remains however open. Here we study enhanced heat transfer by a model junction immersed between two thermal baths at different temperatures T_h and T_c ($T_h > T_c$). The transferred heat power is enhanced via controlling the junction by means of external time-dependent fields. Provided that the spontaneous heat flow process is optimized over the junction Hamiltonian, any enhancement of this spontaneous process does demand consumption and subsequent dissipation of work. The efficiency of enhancement is defined via the increment in the heat power divided over the amount of consumed work. We show that this efficiency is bounded from above by $T_c/(T_h - T_c)$. Formally this is identical to the Carnot bound for the efficiency of ordinary refrigerators which transfer heat from cold to hot. It also shares some (but not all) physical features of the Carnot bound.

I. INTRODUCTION

Heat spontaneously flows from hot to cold. In some cases it is necessary to reverse this flow. Devices that perform this operation need an external input of high-graded energy (work), which is lost in the process: refrigerators cool a colder body in the presence of a hotter environment, while heaters heat up a hot body in the presence of a colder one [1]. The efficiency (or coefficient of performance) of these devices is naturally defined as the useful effect—for refrigerators this is the heat extracted from the colder body, while for heaters this is the heat delivered to the hotter body—divided over the work consumed per cycle from the work-source [1]. The first and second laws of thermodynamics limit this efficiency from above by the Carnot value: For a refrigerator (heater) operating between two thermal baths at temperatures T_c and T_h, respectively, the Carnot efficiency reads [1]

$$\zeta_{\text{refrigerator}} = \frac{\theta}{1-\theta}, \quad \zeta_{\text{heater}} = \frac{1}{1-\theta}, \quad \theta \equiv \frac{T_c}{T_h} < 1. \,(1)$$

There are however situations, where the spontaneous direction of the process is the desired one, but its power has to be increased. An example of such a process is perspiration (sweating) of mammals [2]. A warm mammalian body placed in a colder environment will naturally cool due to spontaneous heat transfer from the body surface. Three spontaneous processes are involved in this: infrared radiation, conduction and convection [2]. When the environmental temperature is not very much lower than the body temperature, the spontaneous processes are not sufficiently powerful, and the sweating mechanism is switched on: sweating glands produce water, which during evaporation absorbs latent heat from the body surface and thus cools it [2]. Some amount of free energy (work) is spent in sweating glands to wet the body surface. Similar examples of heat transfer are found in the field of industrial heat-exchangers, where the external source of work is employed for mixing up the heat-exchanging fluids.

The main feature of these examples is that they combine spontaneous and driven processes. Both are macroscopic, and with both of them the work invested in enhancing the process is ultimately consumed and dissipated. Pertinent examples of enhanced transport exist in biology [4, 5]. During enzyme catalysis, the spontaneous rate of a chemical reaction is increased due to interaction of the corresponding enzyme with the reaction substrate. (A chemical reaction can be regarded as particle transfer from a higher chemical potential to a lower one.) There are situations where enzyme catalysis is fueled by external sources of free energy supplied by co-enzymes [4]. However, many enzymes function autonomously and cyclically: The enzyme gathers free energy from binding to the substrate, stores this free energy in slowly relaxing conformational degrees of freedom [6, 7], and then employs it for lowering the activation barrier of the reaction thereby increasing its rate [4–7]. Overall, no free energy (work) is consumed for enhancing the process within this scenario. Similar situations are realized in transporting hydrophilic substances across the cell membrane [4]. Since these substances are not soluble in the membrane, their motion along the (electro-chemical) potential gradient is slow, and special transport proteins are employed to enhance it [4, 5]. Such a *facilitated diffusion* normally does not consume free energy (work).

These examples of enhanced processes motivate us to ask several questions. Why is that some processes of enhancement employ work consumption, while others do not? When enhancement does (not) require work consumption and dissipation? If the work-consumption does take place, how to define the efficiency of enhancement, and are there bounds for this efficiency comparable to (1)? These questions belong to thermodynamics of enhanced processes, and they are currently open. Laws of thermodynamics do not answer to them directly, be-

cause here the issue is in increasing the rate of a process. Dealing with time-scales is a weak-point of the general thermodynamic reasoning [3], a fact that motivated the development of finite-time thermodynamics [8].

Here we address these questions via analysing a quantum model for enhanced heat transfer. The model describes a few-level junction immersed between two thermal baths at different temperatures; see section II. The junction is subjected to an external field, which enhances the heat transferred by the junction along its spontaneous direction. The virtue of this model is that the optimization of the transferred heat over the junction Hamiltonian can be carried out explicitly. Based on this, we determine under which conditions the enhancement of heat-transfer does require work-consumption. We also obtain an upper bound on the efficiency of enhancement, which in several aspects is similar to the Carnot bound (1).

Heat flow in microscale and nano-scale junctions received much attention recently [9–16, 19]. This is related to the general trend of technologies towards smaller scales. Needless to stress that thermodynamics of enhanced heat-transfer is relevant for this field, because it should ultimately draw the boundary beetween what is possible and what is not when cooling a hot body in the presence of a colder one. Brownian pumps is yet another field, where external fields are used to drive transport; see, e.g., [20, 21] and references therein. Some of the setups studied in this field are not far from the enhanced heat transport investigated here. However, thermodynamical quantities (such as work and enhancement efficiency) were so far not studied for these systems, though thermodynamics of Brownian motors [work-extracting devices] is a developed subject reviewed in [22].

The rest of this paper is organized as follows. The model of heat-conducting junction is introduced in section II. Section III shows how the transferred heat (with and without enhancing) can be optimized over the junction structure. The efficiency of enhancing is studied in section IV. Section V discusses how some of the obtained results can be recovered from the formalism of linear non-equilibrium thermodynamics. We summarize in section VI. Several questions are relegated to Appendices.

II. THE MODEL

Our model for the heat pump (junction) consists of two quantum systems $\mathbf{H}$ and $\mathbf{C}$ with Hamiltonians $H_{\mathbf{H}}$ and $H_{\mathbf{C}}$, respectively; see Fig. 1. Each system has n energy levels and couples to its thermal bath. Similar models were employed for studying heat engines [17, 18] and refrigerators [19]. It will be seen below that this model admits a classical interpretation, because all the involved initial and final density matrices will be diagonal in the energy representation. We shall however work within the quantum framework, since it is more intuitive.

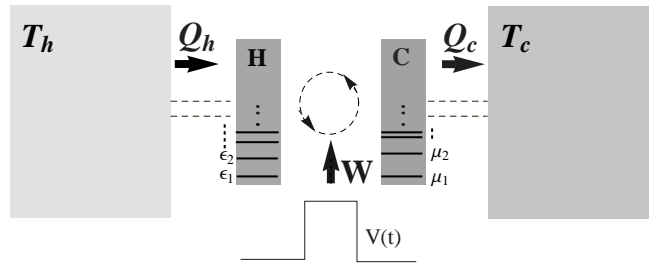Initially, $\mathbf{H}$ and $\mathbf{C}$ do not interact with each other. Due to coupling with their baths they are in equilibrium at

FIG. 1: The heat pump model. The few-level systems $\mathbf{H}$ and $\mathbf{C}$ operate between two baths at temperatures T_c and T_h $T_c < T_h$. During the first step of operation the two systems interact together either spontaneously or driven by a work-source at the cost of work W. During this stage couplings with the thermal baths is neglected (thermal isolation). In the second step the systems $\mathbf{H}$ and $\mathbf{C}$ do not interact with each other and freely relaxes to their equilibrium states (2) under action of the corresponding thermal bath.

temperatures $T_h = 1/\beta_h > T_c = 1/\beta_c$ [we set $k_{\mathrm{B}} = 1$]:

$$\rho = e^{-\beta_h H_{\mathbf{H}}}/\mathrm{tr}\left[e^{-\beta_h H_{\mathbf{H}}}\right], \quad \sigma = e^{-\beta_c H_{\mathbf{C}}}/\mathrm{tr}\left[e^{-\beta_c H_{\mathbf{C}}}\right], \quad (2)$$

where ρ and σ are the initial Gibbsian density matrices of $\mathbf{H}$ and $\mathbf{C}$, respectively. We write

$$\rho = \mathrm{diag}[r_n, ..., r_1], \qquad \sigma = \mathrm{diag}[s_n, ..., s_1], \qquad (3)$$
$$H_{\mathbf{H}} = \mathrm{diag}[\varepsilon_n, ..., \varepsilon_1 = 0\,], \quad H_{\mathbf{C}} = \mathrm{diag}[\mu_n, ..., \mu_1 = 0\,],$$

where $\mathrm{diag}[a, .., b]$ is a diagonal matrix with entries $(a, ..., b)$, and where without loss of generality we have nullified the lowest energy level of both $\mathbf{H}$ and $\mathbf{C}$. Thus the overall initial density matrix is

$$\Omega_{\mathrm{in}} = \rho \otimes \sigma, \qquad (4)$$

and the initial Hamiltonian of the junction is

$$H_0 = H_{\mathbf{H}} \otimes 1 + 1 \otimes H_{\mathbf{C}}. \qquad (5)$$

A. Spontaneous operation

During a spontaneous process no work is exchanged with external sources. For our situation a spontaneous heat transfer will amount to a certain interaction between $\mathbf{H}$ and $\mathbf{C}$. Following to the approach of [24–26] we model this interaction via a Hamiltonian that conserves the (free) Hamiltonian H_0 [see (5)] for all interaction times. This then realizes the main premise of spontaneous processes: no work exchange at any time. Our model for spontaneous heat transfer consists of two steps.

1. During the first step $\mathbf{H}$ and $\mathbf{C}$ interact with each other [collision]. We assume that this interaction takes a sufficiently short time δ, and during this time the coupling with the two thermal baths can be neglected [thermal isolation]. The interaction is described by the Hamiltonian H_{int} added to (5):

$$H = H_{\mathbf{H}} \otimes 1 + 1 \otimes H_{\mathbf{C}} + H_{\mathrm{int}}. \qquad (6)$$

The overall Hamiltonian H again lives in the n^2-dimensional Hilbert space of the junction [1].

As argued above, the interaction Hamiltonian commutes with the total Hamiltonian:

$$[H_0, H_{\text{int}}] = 0, \qquad (7)$$

making the energy H_0 a conserved quantity [2]. To have a non-trivial effect on the considered system, the interaction Hamiltonian H_{int} should not commute with the separate Hamiltonian: $[H_{\mathbf{H}} \otimes 1, H_{\text{int}}] \neq 0$. For this to be the case the spectrum of H_0 should contain at least one degenerate eigenvalue. Otherwise, relations $[H_0, H_{\text{int}}] = 0$ and $[H_{\mathbf{H}} \otimes 1, H_0] = 0$ will imply $[H_{\mathbf{H}} \otimes 1, H_{\text{int}}] = 0$ (and thus a trivial effect of H_{int}), because the eigen-base of H_0 will be unique (up to re-numbering of its elements and their multiplication by phase factors). The energy

$$Q_h^{[\text{sp}]} = \text{tr}\left(H_{\mathbf{H}} \left[\rho - \text{tr}_{\mathbf{C}} \left(e^{-\frac{i\delta}{\hbar} H_{\text{int}}} \, \Omega_{\text{in}} \, e^{\frac{i\delta}{\hbar} H_{\text{int}}} \right) \right] \right), \quad (8)$$

lost by $\mathbf{H}$ during the interaction is gained by $\mathbf{C}$. Here $\text{tr}_{\mathbf{H}}$ and $\text{tr}_{\mathbf{C}}$ are the partial traces.

Commutative interaction Hamiltonians (7) are applied to studying heat transfer in [24–26]. Refs. [24, 25] are devoted to supporting the thermodynamic knowledge via quantum Hamiltonian models. In contrast, the approach of [26] produced new results.

2. For times larger than δ, $\mathbf{H}$ and $\mathbf{C}$ do not interact and freely relax back to their equilibrium states (2, 4) due to interaction with the corresponding thermal baths. These equilibrium states are reached after some relaxation time τ. Thus the cycle is closed—the junction returns to its initial state—and $Q_h^{[\text{sp}]}$ given by (8) is the heat per cycle taken from the hot thermal bath during the relaxation (and thus during the overall cycle).

It should be obvious that once $T_h > T_c$ we get $Q_h^{[\text{sp}]} > 0$: heat spontaneously flow from hot to cold. The proof of this fact is given in [18, 19, 24–26].

For times larger than τ there comes another interaction pulse between $\mathbf{H}$ and $\mathbf{C}$, and the cycle is repeated.

1. Power

Recall that the power of heat-transfer is defined as the ratio of the transferred heat to the cycle duration τ,

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[1] More precisely, we had to write the Hamiltonian (6) as $H_{\mathbf{H}} \otimes 1 + 1 \otimes H_{\mathbf{C}} + \alpha(t) H_{\text{int}}$, where $\alpha(t)$ is a switching function that turns to zero both at the initial and final time. This will however not alter the subsequent discussion in any serious way.

[2] This implementation of spontaneous heat-transfer processes admits an obvious generalization: one need not require the conservation of H_0 for all interaction times, it suffices that no work is consumed or released within the overall energy budget of the process in the time-interval $[0, \delta]$. For our purposes this generalization will not be essential; see (27).

$Q_h^{[\text{sp}]}/\tau$. For the present model τ is mainly the duration of the second stage, i.e., τ is the relaxation time, which depends on the concrete physics of the system-bath coupling. For a weak system-bath coupling τ is larger than the internal characteristic time of $\mathbf{H}$ and $\mathbf{C}$. In contrast, for the collisional system-bath interaction, τ can be very short; see Appendix A. Thus the cycle time τ is finite, and the power $Q_h^{[\text{sp}]}/\tau$ does not vanish due to a large cycle time, though it can vanish due to $Q_h^{[\text{sp}]} \to 0$.

Note that some entropy is produced during the free relaxation. This entropy production can be expressed via quantities introduced in (4–8); see [19] for details. The first step does not produce entropy, because it is thermally isolated and is realized by a unitary operation that can be reversed by operating only on observable degrees of freedom ($\mathbf{H} + \mathbf{C}$). It is seen that no essential aspect of the considered model depends on details of the system-bath interaction. This is an advantage.

B. Driven operation

The purpose of driving the junction with an external field is to enhance [increase] the spontaneous heat $Q_h^{[\text{sp}]}$. The driven regime reduces to the above two steps, but instead of the spontaneous interaction we have the following situation: the interaction between $\mathbf{H}$ and $\mathbf{C}$ is induced by an external work-source. Thus (7) does not hold anymore. The overall interaction [between $\mathbf{H}$, $\mathbf{C}$ and the work-source] is described via a time-dependent potential $V(t)$ in the total Hamiltonian

$$H_{\mathbf{H}} \otimes 1 + 1 \otimes H_{\mathbf{C}} + V(t) \qquad (9)$$

of $\mathbf{H} + \mathbf{C}$. The interaction process is still thermally isolated: $V(t)$ is non-zero only in a short time-window $0 \leq t \leq \delta$ and is so large there that the influence of the couplings to the baths can be neglected.

Thus the dynamics of $\mathbf{H} + \mathbf{C}$ is unitary for $0 \leq t \leq \delta$:

$$\Omega_{\text{f}} \equiv \Omega(\delta) = \mathcal{U} \, \Omega_{\text{i}} \, \mathcal{U}^{\dagger}, \quad \mathcal{U} = \mathcal{T} e^{-\frac{i}{\hbar} \int_0^\delta \text{d}s [V(s) + H_0]}, \quad (10)$$

where $\Omega_{\text{i}} = \Omega(0) = \rho \otimes \sigma$ is the initial state defined in (2), Ω_{f} is the final density matrix, $\mathcal{U}$ is the unitary evolution operator, and where $\mathcal{T}$ is the time-ordering operator. The work put into $\mathbf{H} + \mathbf{C}$ reads [1, 3]

$$W = E_{\text{f}} - E_{\text{i}} = \text{tr}\left[\left(H_{\mathbf{H}} \otimes 1 + 1 \otimes H_{\mathbf{C}} \right) \left(\Omega_{\text{f}} - \Omega_{\text{i}} \right) \right], (11)$$

where E_{f} and E_{i} are initial and final energies of $\mathbf{H} + \mathbf{C}$. Due to the interaction, $\mathbf{H}$ ($\mathbf{C}$) looses (gains) an amount of energy Q_h (Q_c)

$$Q_h = \text{tr}(H_{\mathbf{H}}[\rho - \text{tr}_{\mathbf{C}} \, \Omega_{\text{f}}]), \qquad (12)$$

$$Q_c = \text{tr}(H_{\mathbf{C}} [\text{tr}_{\mathbf{H}} \, \Omega_{\text{f}} - \sigma]). \qquad (13)$$

Eqs. (11, 12) imply an obvious relation

$$W = Q_c - Q_h. \qquad (14)$$

Recall that for spontaneous processes not only the consumed work is zero, $W = 0$, but also the stronger conservation condition (7) holds.

Once $\mathbf{H} + \mathbf{C}$ arrives at the final state Ω_{fin}, the intersystem interaction is switched off, and $\mathbf{H}$ and $\mathbf{C}$ separately [and freely] relax to the equilibrium states (2). During this process Q_h is taken as heat from the hot bath, while Q_c is given to the cold bath. Note from section II A 1 that the driven operation does not change the cycle time τ, because the latter basically coincides with the relaxation time. Therefore, increasing Q_h means increasing heat transfer power.

III.   MAXIMIZATION OF HEAT

A.   Maximization variables

The type of questions asked by thermodynamics concerns limiting, optimal characteristics. Sometimes the answers are uncovered directly via the basic laws of thermodynamics, an example being the Carnot bound (1). However, more frequently than not, this goal demands explicit optimization procedures [8].

We shall maximize the heat Q_h transferred from the hot bath over the full Hamiltonian of the junction. For spontaneous processes this amounts to maximizing over Hamiltonian (6) living in the n^2-dimensional Hilbert space of the junction $\mathbf{H} + \mathbf{C}$ and satisfying condition (7). For driven processes we shall maximize over Hamiltonians (9). In this case we shall impose an additional condition that the work put into $\mathbf{H} + \mathbf{C}$ in the first step does not exceed $E > 0$:

$$W \le E. \tag{15}$$

Once the work put into the system is a resource, it is natural to operate with resources fixed from above.

Recall that the Hamiltonians (6, 9) live in the n^2-dimensional Hilbert space. The bath temperatures T_c and T_h and the dimension n^2 (the number of energy levels) will be held fixed during the maximization.

Due to (8) the maximization of the spontaneous heat $Q_h^{[\text{sp}]}$ over the Hamiltonians (6, 7) amounts to maximizing over unitary operators $e^{\frac{i\delta}{\hbar} H_{\text{int}}}$, and over the energies $\{\varepsilon_k\}_{k=2}^n$, $\{\mu_k\}_{k=2}^n$ of $\mathbf{H}$ and $\mathbf{C}$. Likewise, as seen from (9–11), the maximization of the driven heat Q_h amounts to maximizing under condition (15) over all unitary operators $\mathcal{U}$ living in the n^2-dimensional Hilbert space, and over the energies $\{\varepsilon_k\}_{k=2}^n$, $\{\mu_k\}_{k=2}^n$.

We should stress that the class of Hamiltonians living in the n^2-dimensional Hilbert space [with or without constraint (7)] is well-defined due to separating the heat transfer into two steps (thermally isolated interaction and isothermal relaxation). More general classes of processes can be envisaged. For instance, we may write the free Hamiltonian as $H_0 + H_{B,c} + H_{B,h}$, where H_0, $H_{B,c}$ and $H_{B,h}$ are, respectively, the Hamiltonians of the

junction and the two thermal baths. Now the Hamiltonian H_{int} of spontaneous processes will be conditioned as $[H_{\text{int}}, H_0 + H_{B,c} + H_{B,h}] = 0$. This condition is more general than (7). Then the corresponding class of driven processes can be naturally defined via the same class of Hamiltonians but without this commutation condition. We do not consider here such general processes, since we are not able to optimize them.

B.   Unconstrained maximization

As seen below, the maximization of the spontaneously transferred heat (8) amounts to a particular case of maximizing Q_h. So we shall directly proceed to maximizing the driven heat Q_h; see (12).

First, take in (15) the simplest case: $E = +\infty$. This case contains the pattern of the general solution. Here we have no constraint on maximization of Q_h and it is done as follows. Since $\text{tr}[H_{\mathbf{H}}\rho]$ depends only on $\{\varepsilon_k\}_{k=2}^n$, we choose $\{\mu_k\}_{k=2}^n$ and $V(t)$ so that the final energy $\text{tr}[H_{\mathbf{H}} \, \text{tr}_{\mathbf{C}}\Omega_{\text{f}}]$ attains its minimal value zero. Then we shall maximize $\text{tr}[H_{\mathbf{H}}\rho]$ over $\{\varepsilon_k\}_{k=2}^n$. Note from (3)

$$
\begin{aligned}
H_{\mathbf{H}} \otimes 1 &= \text{diag}[\varepsilon_1, \ldots, \varepsilon_1, \ldots, \varepsilon_n, \ldots, \varepsilon_n], \\
\Omega_{\text{i}} = \rho \otimes \sigma &= \text{diag}[r_1 s_1, \ldots, r_1 s_n, \ldots, r_n s_1, \ldots, r_n s_n].
\end{aligned}
$$

It is clear that $\text{tr}[H_{\mathbf{H}} \, \text{tr}_{\mathbf{C}}\Omega_{\text{f}}] = \text{tr}[(H_{\mathbf{H}} \otimes 1)\mathcal{U}\Omega_{\text{i}}\mathcal{U}^{\dagger}]$ goes to zero when, e.g., $s_2 = \ldots = s_n \to 0$ ($\mu \equiv \mu_2 = \ldots = \mu_n \to \infty$), while $\mathcal{U}$ amounts to the SWAP operation $\mathcal{U}\rho \otimes \sigma\mathcal{U}^{\dagger} = \sigma \otimes \rho$. Simple symmetry considerations show that at the maximum of the initial energy $\text{tr}[H_{\mathbf{H}}\sigma]$ the second level is $n-1$ fold degenerate, i.e. $\varepsilon \equiv \varepsilon_2 = \ldots = \varepsilon_n$. Denoting

$$u = e^{-\beta_h \varepsilon} \propto r_2 = .. = r_n \tag{16}$$

we obtain for $Q_h = \mathcal{Q}_h(\infty)$

$$\mathcal{Q}_h(\infty) = T_h \ln\left(\frac{1}{u}\right)\left[1 - \frac{1}{1 + (n-1)u}\right] \tag{17}$$

where u is to be found from maximizing the RHS of (17) over u, i.e., u is determined via

$$1 + (n-1)u + \ln u = 0. \tag{18}$$

Note that in this case $W = +\infty$. In the $n \gg 1$ limit we have $u = \frac{\ln n}{n}[1 + o(1)]$ from (18) and $Q_h = T_h \ln n \left[1 + \mathcal{O}\left(\frac{\ln \ln n}{\ln n}\right)\right]$.

C.   Constrained maximization

The case of a finite E in (15) is more complicated. We had to resort to numerical recipes of Mathematica 6. Denoting $\{|i_{\mathbf{H}}\rangle\}_{k=1}^n$ and $\{|i_{\mathbf{C}}\rangle\}_{k=1}^n$ for the eigenvectors of $H_{\mathbf{H}}$ and $H_{\mathbf{C}}$, respectively, we see from (11, 12) that W and Q_h feel $\mathcal{U}$ only via the matrix

$$C_{ij\,|\,kl} = |\langle i_{\mathbf{H}} j_{\mathbf{C}}|\mathcal{U}|k_{\mathbf{H}} l_{\mathbf{C}}\rangle|^2. \tag{19}$$
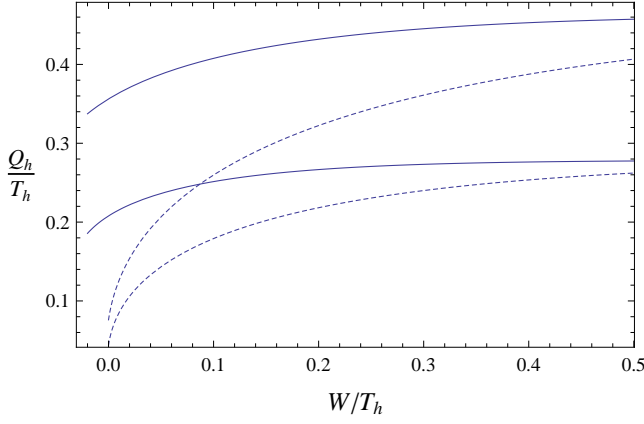
FIG. 2: The optimal transferred heat $\mathcal{Q}_h$ versus work W. Dashed curves refer to $\theta \equiv T_c/T_h = 0.9$: $n = 2$ (lower dashed curve) and $n = 3$ (upper dashed curve). Normal curves refer to $\theta = 0.5$: $n = 2$ (lower normal curve) and $n = 3$ (upper normal curve).

This matrix is double-stochastic [23]:

$$\sum_{ij} C_{ij\,|\,kl} = \sum_{kl} C_{ij\,|\,kl} = 1. \tag{20}$$

Conversely, for *any* double-stochastic matrix $C_{ij\,|\,kl}$ there is *some* unitary matrix U with matrix elements $U_{ij\,|\,kl}$, so that $C_{ij\,|\,kl} = |U_{ij\,|\,kl}|^2$ [23]. Thus, when maximizing various functions of W and Q_c over the unitary $\mathcal{U}$, we can directly maximize over the $(n^2 - 1)^2$ independent elements of $n^2 \times n^2$ double stochastic matrix $C_{ij\,|\,kl}$. This fact simplifies the problem.

Numerical maximization of Q_h over all unitaries $\mathcal{U}$—alternatively, over all doubly stochastic C matrices (19)—and energy spectra $\{\mu_k\}_{k=2}^n$ and $\{\varepsilon_k\}_{k=2}^n$ constrained by $W \leq E$ produced the following results:

- The upper energy levels for both systems $\mathbf{H}$ and $\mathbf{C}$ are $n - 1$ times degenerate [see (3)]:

$$\mu = \mu_2 = \ldots = \mu_n, \quad \varepsilon = \varepsilon_2 = \ldots = \varepsilon_n. \tag{21}$$

- The optimal unitary corresponds to SWAP:

$$\mathcal{U}\rho \otimes \sigma \mathcal{U}^\dagger = \sigma \otimes \rho. \tag{22}$$

- The work resource is exploited fully, i.e., the maximal Q_h is reached for $W = E$.

Though we have numerically checked these results for $n \leq 5$ only, we trust that they hold for an arbitrary n.

Denoting by $\mathcal{Q}_h$ the maximal value of Q_h, and introducing from (21)

$$v = e^{-\beta_c \mu} \quad \text{and} \quad u = e^{-\beta_h \varepsilon}, \tag{23}$$

we have

$$\frac{\mathcal{Q}_h}{T_h} = \ln\left[\frac{1}{u}\right] \frac{(n-1)(u-v)}{[1 + (n-1)v]\,[1 + (n-1)u]}, \tag{24}$$

$$\frac{W}{T_h} = \frac{(\ln u - \theta \ln v)\,(n-1)(u-v)}{[1 + (n-1)v]\,[1 + (n-1)u]}, \tag{25}$$

where u and v in (24, 25) are determined from maximizing the RHS of (24) and satisfying constraint (25).

An important implication of (24, 25) is that $\mathcal{Q}_h(W)$ is an increasing function of W for all allowed values of W:

$$\mathcal{Q}_h(W) > \mathcal{Q}_h(W') \quad \text{if} \quad W > W'. \tag{26}$$

Fig. 2 illustrates this fact. For fixed parameters T_c, T_h and n, the allowed W's range from a certain negative value—which corresponds to work-extraction from a two-temperature system $\mathbf{H} + \mathbf{C}$—to arbitrary $W > 0$. Eq. (26) expresses an intuitively expected, but still nontrivial fact that the best transfer of heat takes place upon consuming most of the available work. Note that this result holds only for properly optimized values of $\mathcal{Q}_h$. One can find non-optimal set-ups, where (26) is not valid [3].

D. Optimization of spontaneous processes

According to our discussion in section II A, the maximization of transferred heat $Q_h^{[\mathrm{sp}]}$ given by (8) should proceed over all unitary operators $e^{-\frac{i\delta}{\hbar}H_{\mathrm{int}}}$ with H_{int} satisfying (7) and over the energies $\{\varepsilon_k\}_{k=2}^n$, $\{\mu_k\}_{k=2}^n$ of $\mathbf{H}$ and $\mathbf{C}$. This maximization has been carried out along the lines described around (20). We obtained that the maximal spontaneous heat $\mathcal{Q}_h^{[\mathrm{sp}]}$ is equal to $\mathcal{Q}_h$ in (24) under condition $W = 0$:

$$\mathcal{Q}_h^{[\mathrm{sp}]} = \mathcal{Q}_h(W = 0). \tag{27}$$

Thus the optimal spontaneous processes coincide with optimal processes with zero consumed work. This result is non-trivial, because the class of unitary operators with $W = 0$ is larger than the class of unitary operators $e^{-\frac{i\delta}{\hbar}H_{\mathrm{int}}}$ with H_{int} satisfying (7). Nevertheless, these two classes produce the same maximal heat.

- Eqs. (26, 27) imply that if the spontaneous heat transfer process is already optimal (with respect to the junction Hamiltonian) its enhancement with help of driven processes does demand work-consumption, $W > 0$. This fact is non-trivial, because—as well known from the theory of heat-engines—also work-extraction does lead to the heat flowing from cold to hot [1, 3].

Taking $W = 0$ in (24, 25) and recalling (23) we get

$$\mu = \varepsilon, \qquad u = v^\theta. \tag{28}$$

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[3] The simplest example is a junction, where the free Hamiltonian H_0 has a non-degenerate energy spectrum, and thus the condition (7) does not hold. There are no proper spontaneous processes for this case. Still there can exist a work-exracting ($W < 0$) driven processes that transfer heat from hot to cold.
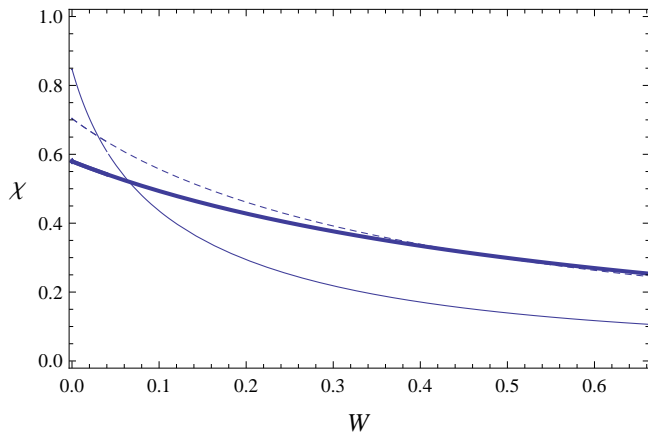
FIG. 3: The efficiency χ versus work W for $\theta \equiv T_c/T_h = 0.5$ and $n = 2$ (normal curve), $n = 10$ (dashed curve) and $n = 30$ (thick curve).

The interpretation of (28) is that since there are only two independent energy gaps in the system, they have to be precisely matched for the spontaneous processes to be possible; see in this context the discussion after (7). Thus the spontaneous heat $\mathcal{Q}_h^{[\mathrm{sp}]}$ is given as

$$\frac{\mathcal{Q}_h^{[\mathrm{sp}]}}{T_c} = \ln\left[\frac{1}{v_0}\right]\frac{(n-1)(v_0^\theta - v_0)}{[1+(n-1)v_0^\theta][1+(n-1)v_0]}, \quad (29)$$

where v_0 maximizes the RHS of (29).

E. How much one can enhance the spontaneous process?

We would like to compare the optimal spontaneous heat (29) with the optimal heat $\mathcal{Q}_h(\infty)$ transferred under consumption of a large amount of work; see (17, 18) and recall (26). One notes that for parameters of Fig. 2 the approximate equality $\mathcal{Q}_h(\infty) \approx \mathcal{Q}_h(W)$ is reached already for $W/T_h < 1$. This figure also shows that for the temperature ratio $\theta \equiv T_c/T_h$ far from 1, the improvement of the transferred heat introduced by driving is not substantial. It is however rather sizable for $\theta \simeq 1$, because here the spontaneous heat (29) is close to zero, while the heat $\mathcal{Q}_h(\infty)$ does not depend on the temperature difference at all; see Fig. 2 and (17, 18).

IV. EFFICIENCY

We saw above that enhancing optimal spontaneous processes does require work. Once this is understood, we can ask how efficient is this work consumption. The efficiency is defined as

$$\chi(W) = \frac{\mathcal{Q}_h(W) - \mathcal{Q}_h^{[\mathrm{sp}]}}{W} > 0, \quad (30)$$

where $\mathcal{Q}_h(W)$ is the optimal heat transferred under condition that the consumed work is not larger than $W > 0$, while $\mathcal{Q}_h^{[\mathrm{sp}]}$ is the optimal spontaneous heat; see (24, 29). Note that the two subtracted quantities $\mathcal{Q}_h(W)$ and $\mathcal{Q}_h^{[\mathrm{sp}]}$ in (30) refer to the same junction $\mathbf{H} + \mathbf{C}$, but with different Hamiltonians; see (24, 25).

For $W \to 0$, $\chi(W)$ increases monotonically and tends to a well defined limit $\chi(0)$; see Fig. 3.

- For fixed θ and n, $\chi(0) = \chi(W \to 0)$ is the maximal possible efficiency at which the enhanced heat pump can operate. As seen from Fig. 3, this maximum is reached for

$$\mathcal{Q}_h(W) - \mathcal{Q}_h(0) \to +0 \quad \text{and} \quad W \to +0, \quad (31)$$

  where we recall that n, T_h and T_c are held fixed.

- There is thus a complementarity between the driven contribution in the heat, which according to (26) maximizes for $W \to \infty$, and the efficiency that maximizes under $W \to 0$.

Note from Fig. 4 the following aspect of the maximal efficiency $\chi(0)$: it decreases for a larger n (and a fixed θ). This is related to the fact that the optimal spontaneous heat $\mathcal{Q}_h^{[\mathrm{sp}]}$ increases for larger n.

- It is seen from Fig. 3 that

$$\chi(W) \le \chi(0) < \frac{\theta}{1-\theta}. \quad (32)$$

  We checked that this upper bound for the efficiency (30) holds for all $\theta = T_c/T_h$ and n.

It will be seen below that the upper bound $\frac{\theta}{1-\theta}$ is reached in the quasi-equilibrium limit $\theta \to 1$. Note that $\frac{\theta}{1-\theta}$ formally coicides with the Carnot limiting efficiency for ordinary refrigerators; see (2). A straightforward implication of (32) is that enhancing optimal spontaneous processes must be inefficient for $\theta \to 0$.

Let us discuss to which extent the bound (32) is similar to the Carnot bound (2) for refrigerators.

0. These two expressions are formally identical.

1. Recall that (2) is a general upper bound for the efficiency of refrigerators that transfer heat against its gradient. Such a transfer does require work-consumption. The same aspect is present in (30), because by its very construction the efficiency (30) refers to enhancement of the optimal spontaneous process that also demands work-consumption. To clarify this point consider a spontaneous process with the transferred heat $Q_h^{[\mathrm{sp}]}$. Let this spontaneous process be non-optimal in the sense that no full optimization over the Hamiltonians (6, 7) has been carried out: $Q_h^{[\mathrm{sp}]} < \mathcal{Q}_h^{[\mathrm{sp}]}$. This non-optimal process is now enhanced via a work-consuming one. Denote by $Q_h(W) > Q_h^{[\mathrm{sp}]}$ the transferred heat of this process, where W is the consumed work. Following (30)
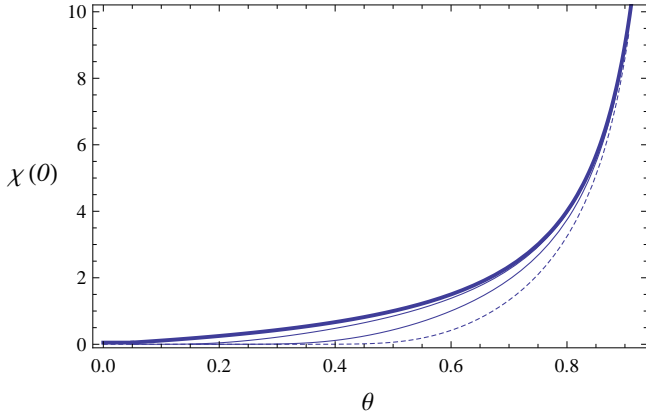
FIG. 4: The maximal efficiency $\chi(0) = \chi(W = 0)$ given by (33) versus $\theta = T_c/T_h$ for $n = 2$ (top normal curve), $n = 101$ (bottom normal curve), and $n = 10^5$ (dotted curve). Thick curve: the efficiency $\theta/(1 - \theta)$.

one can define the efficiency of this enhancement as $\chi'(W) = [Q_h(W) - Q_h^{[\text{sp}]}]/W$. One can now show, see Appendix B, that $\chi'(W)$ can be arbitrary large for a sufficiently small (but non-zero) consumed work W. The reason for this unboundness is that we consider a non-optimal spontaneous process, which can be also enhanced by going to another spontaneous process.

2. We noted above that reaching bound (32) means a negligible enhancement; see (31). The same holds for the Carnot bound (2) for refrigerators: operating sharply at the Carnot efficiency means that the heat transferred during refrigeration is zero; see [19] and references therein.

3. An obvious point where the bounds (32) and (2) differ from each other is that the latter is a straightforward implication of the first and second laws of thermodynamics, while the former is so far obtained in a concrete model only. We opine however that its applicability domain is larger than this model; some support for this opinion is discussed in section V.

A. Efficiency in the quasi-equilibrium limit $\theta \to 1$.

Let us now find a more explicit expression for $\chi(0)$ using the fact of (31). For a small $\frac{W}{T_h}$, (25) implies that u and v are related as $u = v^\theta + x$, with $x = \mathcal{O}[\frac{W}{T_h}]$. Denote the RHS of (24) as $f[u,v]$ and the RHS of (25) as $g[u,v]$. Expand $g[v^\theta + x, v]$ over x, express x via $\frac{W}{T_h}$ and v:

$$x = \frac{W}{T_h} \frac{1}{g'_u[v^\theta, v]},$$

and substitute the obtained result into (24):

$$f[v^\theta, v] + \frac{W}{T_h} \frac{f'_u[v^\theta, v]}{g'_u[v^\theta, v]}.$$

Carrying out the optimization of this quantity over v, we see that in the first order over the small parameter $\frac{W}{T_h}$ the optimal value reads

$$f[v_0^\theta, v_0] + \frac{W}{T_h} \frac{f'_u[v_0^\theta, v_0]}{g'_u[v_0^\theta, v_0]},$$

where v_0 is defined in (29). The final result for the efficiency $\chi(0)$ is $\frac{f'_u[v_0^\theta, v_0]}{g'_u[v_0^\theta, v_0]}$, or

$$\chi(0) = -1 + \theta \ln\left(\frac{1}{v_0}\right)\left[\frac{1}{1 + (n-1)v_0^\theta} - \frac{v_0}{v_0 - v_0^\theta}\right]. \quad (33)$$

Let us now find the asymptotic behaviour of the efficiency (33) for $\theta \to 1$. It is seen from (29) that in this limit $v_0 = a + \mathcal{O}(1 - \theta)$, where a is found from the transcendental equation

$$\ln\frac{1}{a} = 2\frac{1 + (n-1)a}{1 - (n-1)a}. \quad (34)$$

This implies for $\chi(0)$ and $\mathcal{Q}_h^{[\text{sp}]}$:

$$\chi(0) = \frac{\theta}{1 - \theta} - 1 + \frac{2\theta}{1 - (n-1)a} + \mathcal{O}(1 - \theta), \quad (35)$$

$$\mathcal{Q}_h^{[\text{sp}]} = \frac{4T_c(n-1)a(1-\theta)}{(1 - (n-1)a)^2} + \mathcal{O}([1 - \theta]^2). \quad (36)$$

Thus, in the limit $\theta \to 1$ the efficiency χ asymptotically reaches the maximal value $\frac{\theta}{1-\theta}$. This reachability is related to the fact that the spontaneous heat $\mathcal{Q}_h^{[\text{sp}]}$ becomes small; see (36).

Note that the aymptotics (35) is meaningful only for $\theta \to 1$, where $\frac{\theta}{1-\theta}$ is larger than $-1 + \frac{2\theta}{1-(n-1)a}$. For $\ln n \gg 1$, (34) implies asymptotically

$$a(n-1) = 1 - \frac{4}{\ln[n-1]} + \dots. \quad (37)$$

Thus the limits $\theta \to 1$ and $n \gg 1$ do not commute with each other, because the correction term $\frac{2\theta}{1-(n-1)a}$ in (35) will be comparable to the main term $\frac{\theta}{1-\theta}$.

V. ENHANCED HEAT TRANSFER IN LINEAR NON-EQUILIBRIUM THERMODYNAMICS

Since the above results were obtained on a concrete model, one can naturally question their general validity. Here we indicate that these results are recovered from the formalism of linear non-equilibrium thermodynamics [27–29]. This theory deals with two coupled processes: heat transfer between two thermal baths and work done by an external field. In contrast to the model studied in previous sections, the field is not time-dependent; e.g., it can be associated with the chemical potential difference [29]. The difference and similarity between set-ups, where the work is induced by a time-dependent field, and

those where the work is done by a constant field is discussed in [30]. For mesoscopic models which lead to linear non-equilibrium thermodynamics see, e.g., [29, 31].

In the linear regime both the driving field and the temperature difference $T_h - T_c$ are small, so that the heat Q_h and work W can be linearized [27–29]; see also Appendix C. The virtue of this approach is that it is independent from the concrete details of the studied system. The role of a free parameter—over which the setup can be optimized—is played here by the phenomenological coupling between the heat transfer and work input [27].

More specifically, we show in Appendix C that also within the formalism of linear non-equilibrium thermodynamics, enhancing the optimal spontaneous flow requires work-consumption. As for the efficiency, we first recall the message of (35): for $\theta \equiv T_c/T_h \to 1$ the maximal efficiency $\chi(0)$ does not depend on the dimension n^2 of the junction (provided that the latter is fixed) and approaches $\propto 1/(1 - \theta)$. This asymptotic result is to a certain extent universal, because it is also recovered within linear non-equilibrium thermodynamics; see Appendix C. We stress however that only the asymptotics for $\theta \to 1$ is recovered. Since this is a linear theory restricted to a small temperature difference and a small work input, it is naturally not capable of reproducing the full message of the bound (32). For this purpose one would probably need a non-linear thermodynamics theory; see, e.g., [29]. Unfortunately, such theories are not so universal (system-independent) as the linear theory.

VI. SUMMARY

We started this paper by listing several representative examples of enhanced transport and posing two basic questions:

1. When enhancing a spontaneous process does require work-consumption?

2. If such a work-driven enhancement does take place, is there a general bound on its efficiency?

These questions have been answered via a quantum model for a heat-transfer junction immersed between two thermal baths at different temperatures T_c and T_h ($T_c < T_h$). The model is defined in section II. We have chosen to work with this model of junction, because its structure is flexible enough to allow explicit maximization of the transferred heat over the junction Hamiltonian. We thus can determine the maximal heat transferred by the junction.

Our basic results can be stated as follows.

1. When the spontaneous heat-transfer is already maximized over the junction Hamiltonian, its enhancement does require work-consumption.

2. The efficiency is defined with respect to the optimal spontaneous heat transfer as the heat increment due to ehancement divided over the consumed work. This efficiency is shown to be limited from above by $T_c/(T_h - T_c)$, a bound that is reached for $T_c \to T_h$. For this bound to hold it is essential that the efficiency is defined with respect to optimal spontaneous heat transfer. In its turn, the very idea of optimality refers to a class of variables to be optimized over. For the studied model this class is defined by the junctions structure and its Hamiltonian.

The main open problem with these results is whether they hold more generally than the studied model. We presented a partial evidence—partial because it is restricted to a small $T_h - T_c$ within the linear non-equilibrium thermodynamics—that they hold more generally.

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Appendix A: Power of heat transfer

Recall that the power Q_h/τ is defined as the ratio of the transferred heat Q_h to the cycle duration τ. For our model τ is mainly the duration of the second stage, i.e., τ is the relaxation time, which depends on the concrete physics of the system-bath coupling.

We discuss two scenarios of relaxation for the present model. For the collisional relaxation the target system interacts with independent bath particles via successive collisions; see [19, 24, 25]. For our purposes the target system is **H** or **C** that interact with, respectively, the hot and cold bath. Each collision lasts a time $\tau_{\rm col}$, which is much smaller than the characteristic time $\tau_{\rm btw}$ between two collisions. The interaction Hamiltonian [between the target system and a bath particle] is conserved, so that there is no energy cost in switching the system-bath interaction on and off; see [19, 24, 25]. The relaxation time τ can amount to a few $\tau_{\rm btw}$: $\tau_{\rm btw} \lesssim \tau$; see [19].

If now the pulse-time δ of $V(t)$ is also much smaller than $\tau_{\rm btw}$, one realizes a thermally-isolated pulse (since the overlap between the pulse and a collision is negligi-
ble), while the relaxation time τ can be still much smaller than any characteristic time of **C** or **H**. Thus in this scenario the cycle time τ is finite, and the power of heat pumping Q_c/τ does not vanish due to a large cycle time.

Within the second scenario the system-bath interaction is always on, but its magnitude is small [weak-coupling]. Now the relaxation time is much larger than the internal characteristic time of **H** and **C**. Because the system-bath interaction is always on, there will be a contribution in the work (11) coming from the system-bath interaction Hamiltonian. This contribution arises even when the conditions for the pulsed regime hold [18]. However, within the weak coupling assumption this additional contribution is proportional to the square of the system-bath interaction constant and can neglected [18]. We stress that this additional contribution does not arise within the collisional relaxation scenario, because the pulse and collisions are well-separated in time.

Appendix B

Let the system **H** + **C** functions as a *non-optimal* [with respect to the Hamiltonian of **H** + **C**] spontaneous heat pump. The amount of heat transferred per cycle is $Q_h^{\rm [sp]}$. One increases the transferred heat via an external work-source acting on **H** + **C**. Now it is equal to $Q_h > Q_h^{\rm [sp]}$. The amount of work consumed per cycle is W.

The purpose of this Appendix is to show on a concrete example that there is no upper bound on the efficiency:

$$\chi' = \frac{Q_h - Q_h^{\rm [sp]}}{W}. \tag{B1}$$

It can go to $+\infty$ for $W \to +0$.

Let the systems **H** and **C** be three-level systems with Hamiltonians [compare with (3)]

$$H_{\bf H} = {\rm diag}(0, \varepsilon, \varepsilon + \mu), \quad H_{\bf C} = {\rm diag}(0, \mu, \varepsilon + \mu) \tag{B2}$$

where for future purposes we choose $\mu > \varepsilon > 0$. The initial Hamiltonian (5) reads

$${\rm diag}[0, \; \varepsilon, \; \varepsilon + \mu, \; \mu, \; \varepsilon + \mu, \; \varepsilon + 2\mu, \; \varepsilon + \mu, \; 2\varepsilon + \mu, \; 2\varepsilon + 2\mu]$$

The initial state of **H** + **C** is given by (2, 3 4):

$$\rho = \frac{{\rm diag}[1, \; a^\theta, \; a^\theta b^\theta]}{1 + a^\theta + a^\theta b^\theta}, \quad \sigma = \frac{{\rm diag}[1, \; b, \; ab]}{1 + b + ab}, \tag{B3}$$

where we denoted

$$a = e^{-\beta_c \varepsilon}, \quad b = e^{-\beta_c \mu}. \tag{B4}$$

The system **H** + **C** has nine energy levels; three of them have equal energy $\varepsilon + \mu$. Thus spontaneous processes amount to unitary operations that couple these degenerate energy levels to each other, but do not induce transitions to non-degenerate energy levels [compare with

(7)]. Such unitaries will produce double-stochastic matrices of the following form [compare with (19, 20)]

$$C = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & c_{11} & 0 & c_{12} & 0 & c_{13} & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & c_{21} & 0 & c_{22} & 0 & c_{23} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & c_{31} & 0 & c_{32} & 0 & c_{33} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \qquad \text{(B5)}$$

It is not difficult to see that for *fixed energy levels* (B2) the spontanoues process with the largest $Q_h^{[\text{sp}]}$ amounts to $c_{13} = c_{22} = c_{31} = 1$, while other c's nullify. This means that the spontaneous process interchanges populations of the third and seventh energy levels; see (B3). The heat transferred per cycle reads

$$Q_h^{[\text{sp}]} = \frac{1}{z}\left[a^\theta b^\theta - ab\right](\varepsilon + \mu), \qquad \text{(B6)}$$

$$z \equiv (1 + a + ab)\left(1 + a^\theta + a^\theta b^\theta\right). \qquad \text{(B7)}$$

Now the external field acts on the system $\mathbf{H} + \mathbf{C}$ enhancing the heat transfer, i.e., increasing $Q_h^{[\text{sp}]}$. We postulate that this action amounts to SWAP transformation. We obtain for the heat, work and efficiency (B1) [compare with (12, 11)]:

$$Q_h = \frac{1}{z}\{\varepsilon\left[a^\theta - b + ba^\theta(a - b^\theta)\right]$$
$$+(\varepsilon + \mu)\left[(ab)^\theta - ab + ba^\theta(b^\theta - a)\right]\},$$
$$W = \frac{1}{z}(\mu - \varepsilon)\left[a^\theta - b - ba^\theta(b^\theta - a)\right]$$

It is seen that when $\varepsilon \to \mu$ [which means $a \to b + 0$] the difference $Q_h - Q_h^{[\text{sp}]}$ is positive and finite, while the work W is positive, but turns to zero as $W \propto \mu - \varepsilon$. Thus if one defines efficiency as $\chi' = (Q_h - Q_h^{[\text{sp}]})/W$, it will turn to infinity for $\varepsilon \to \mu$. The divergence of χ' is ultimately due to the fact that the spontaneous heat was maximized over Hamiltonian (6) only partially, i.e., it was not maximized over the energy levels of $\mathbf{H}$ and $\mathbf{C}$.

Appendix C: Heat-transfer enhancement from linear non-equilibrium thermodynamics

The formalism of linear non-equilibrium thermodynamics starts by introducing currents of physical quantities J_i (e.g., currents of energy or mass) and the respective conjugate forces X_i [27, 28]. We introduce two such currents and forces:

$$J_1, \ J_2, \ X_1, \ X_2. \qquad \text{(C1)}$$

J_1 will refer to heat flowing from the high-temperature bath at temperature $T_h = 1/\beta_h$ to the lower one at temperature $T_c = 1/\beta_c$, while the second current J_2 is the work done by an external time-independent force. Thus

$$X_1 = \beta_c - \beta_h = \frac{T_h - T_c}{T^2}, \quad X_2 = \frac{f}{T}, \quad T \equiv \sqrt{T_h T_c}, \text{(C2)}$$

where f is the force responsible for the work [28]. Once we are in the linear regime over small parameters $T_h - T_c$ and f, one can substitute T in (C2) by T_c or T_h; the choice of T is conventional.

In essence, linearity means that the state which supports the currents is not far from equilibrium [28]. The basic postulate of this formalism is linear relations between currents and forces [28]:

$$J_1 = L_{11}X_1 + L_{12}X_2, \qquad J_2 = L_{21}X_1 + L_{22}X_2. \ \text{(C3)}$$

where the kinetic coeffcients L_{ik} do not depend on X_i due to assumed linearity of the overall process. The kinetic coeffcients L_{12} and L_{21} quantify the coupling between the two processes.

The statement of the second law relevant for this composite linear process amounts to the positivity of entropy production $d_i S/dt$ [28]

$$\frac{d_i S}{dt} = X_1 J_1 + X_2 J_2 = \sum_{i,k=1}^{2} L_{ik}X_i X_k \geq 0. \qquad \text{(C4)}$$

As a consequence of the time-invariance of the underlying microscopic theories (i.e., classical or quantum mechanics), the matrix of kinetic coefficients is symmetric [28]

$$L_{12} = L_{21}. \qquad \text{(C5)}$$

We now assume that some work is dissipated, $J_2 > 0$, for enhancing the heat flow. The spontaneous heat transfer corresponds to no coupling between the processes: $L_{12} = L_{21} = 0$.

In calculating the efficiency of enhancement we shall follow the same strategy as in sections III and IV: first we shall maximize the transferred heat J_1 under a fixed amount of work $W = fJ_2 = TX_2 J_2$. Then the efficiency will be defined as in (30). The maximization variables are f, L_{11}, L_{22} and $L_{12} = L_{21}$. The temperatures T_c and T_h are held fixed; see also (C2). Write J_1 as

$$J_1 = L_{11}X_1 + \frac{W}{TX_1} - L_{22}\frac{X_2^2}{X_1}. \qquad \text{(C6)}$$

During the maximization we should keep L_{11} confined by some upper limit $\mathcal{L}_{11}$; otherwise J_1 will not be finite. Eq. (C5), which should hold for arbitrary X_1 and X_2, implies $L_{22} \geq 0$. Recaling that also $X_1 > 0$, we see that J_1 is maximized for $L_{11} = \mathcal{L}_{11}$ and $L_{22} = 0$:

$$\mathcal{J}_1 = \mathcal{L}_{11}X_1 + \frac{W}{TX_1}. \qquad \text{(C7)}$$

Thus for enhancing the optimal spontaneous heat $\mathcal{L}_{11}X_1$ we need $W > 0$ (work-consumption). Subtracting from

$\mathcal{J}_1$ the spontaneous contribution $\mathcal{L}_{11}X_1$ and dividing over the consumed work W, we get for the efficiency:

$$\chi = \frac{1}{TX_1} = \frac{T}{T_h - T_c}, \qquad (\text{C8})$$

which for a small temperature difference $T_h - T_c$ (recall that this is the applicability domain of the considered linear theory) coincides with (35).